

Materials Processing using an Atmospheric-Pressure Plasma Jet

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Abstract

Processing materials at atmospheric pressure provides clear advantages over traditional, vacuum-based plasma processing. In addition to reducing the capital cost of equipment and eliminating constraints imposed by vacuum-compatibility, high-pressure and low-temperature plasma processes offer unprecedented improvements for the generation of active chemical species, high chemical selectivity, minimal ion densities that result in low surface damage, and surface-treatment methods unattainable by other means. We describe several variations of this unique plasma source and some of its potential applications.

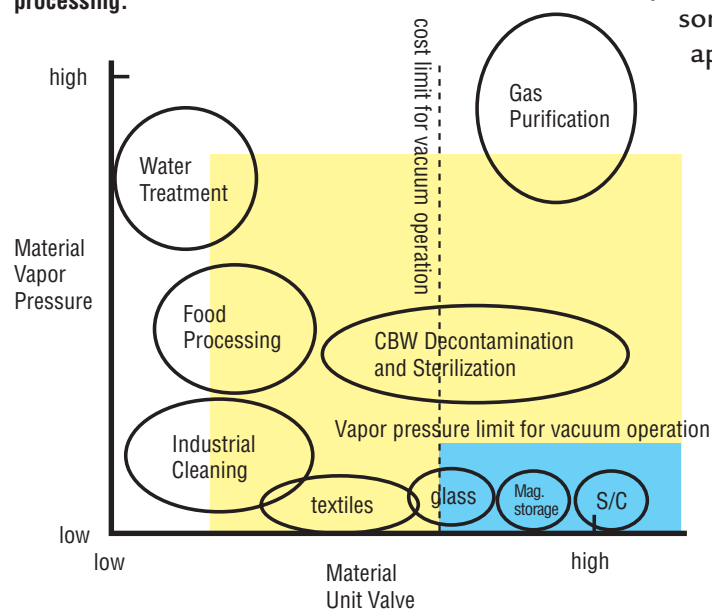
Introduction

Plasmas have been extensively used for materials-processing applications for the past 30 years.¹ Yet, these applications have generally been limited to select, high “value-added” uses, such as steps required for manufacture of semiconductor devices, magnetic media, or deposition of energy-efficient films for architectural glass. In these applications, plasmas are used because they provide a rich source of chemically active species that react with a surface, or which react with each other to produce secondary, short-lived chemical precursors needed for thin-film deposition. The success of plasma processing technology stems from its low-temperature operation and the fact that no other method can provide the same nondestructive, materials-treatment capability. As such, plasmas are typically used for selective film etching, surface treatment to enhance wettability or to improve adhesion, and in the manufacture of thin films, including diamond-like carbon (DLC), and films having desired metallic, dielectric, or other composite properties.

But, what happens when traditional plasma treatment methods overlap conventional means of surface treatment, such as cleaning applications, or when vacuum-based processing presents obstacles, such as in sterilization or food treatment? In these cases, plasma processing often fails, either because the operation cost for the plasma-based method exceeds the cost for an alternative method or because the demands imposed by vacuum processing are excessive. This case is more the rule than the exception, as demonstrated in Figure 1.

Figure 1 shows two major constraints that arise for traditional, vacuum-based plasma processing: (1) the physical pressure limit required for operation of the plasma, and (2) the economic constraint imposed by this plasma treatment process. The first constraint arises from the need for vacuum operation in order to achieve plasma generation that is nondestructive to materials; the second constraint comes from the fact that the combined processing cost (*i.e.*, the cost of consumables plus the amortized capital cost)

Figure 1. Comparison of the process limits that result from vapor pressure and economic constraints for both vacuum and atmospheric-pressure plasma processing. The rectangular box in the lower right corner represents the domain for vacuum processing. The larger box represents the domain constraints for atmospheric-pressure plasma processing. The larger box also contains much of the process domain represented for vacuum-based plasma processing.



must remain within a level acceptable to the customer. If both constraints cannot be simultaneously met, then the process is infeasible.

The capital equipment cost and the high operation and maintenance costs required for vacuum-processing results in the relatively limited domain illustrated by the small crosshatched (blue) region in the lower right hand corner of Figure 1.

This figure shows that vacuum-compatible, high-value items, such as semiconductors, magnetic media, and specialty films used in architectural glass, are suitable opportunities for vacuum-based plasma processing. In contrast, the larger crosshatched (yellow) region in Figure 1 illustrates the domain available for atmospheric-pressure plasma processing. The greater domain available to this technology

results from a higher vapor-pressure limit and the lower materials-processing cost associated from operation outside of vacuum at normal pressure. Even opportunities such as water and wastewater treatment pose potential opportunities for plasma processing—provided that the materials-processing cost is acceptably low. Of course, developments that reduce the materials-

processing costs will change these results. Figure 1 is intended for qualitative comparison.

Table 1 illustrates some of the applications associated with the materials processes shown in Figure 1. Clearly, a broad range of treatment opportunities exists. For simplicity, only several examples are shown below. Several of these processes are illustrated diagrammatically in Figure 2.

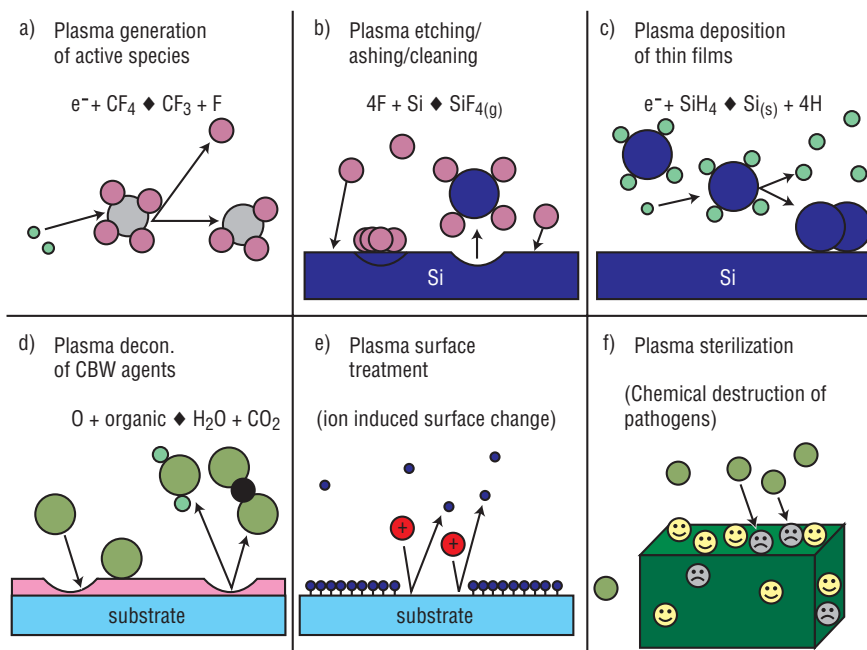


Figure 2. An illustration of several of the fundamental processes used in plasma processing of materials. Some are purely chemical in nature; some involve physical contributions, such as the impact of ions with the surface. Combinations of both chemical and physical processes are common.

Table 1. A Brief Compilation of Various Plasma/Surface Interactions and the Active Component of the Plasma that Contributes to the Desired Product or Change Material/Substrate Plasma Component Desired Product

| Material/Substrate | Plasma Component | Desired Product |
|---|---|--|
| Semiconductor substrates | Active neutral and ionic species generated by electron impact | Etching, thin film deposition, stripping, cleaning |
| Magnetic Storage Media | Sputtered atoms generated by ion bombardment of the target | Magnetic thin films, anti-corrosive coatings |
| Glass | Thin film chemical precursors, neutrals | Energy efficient coatings |
| Textiles | Ion bombardment, active neutrals | Increased wettability, wear properties, |
| Industrial Cleaning | Oxygen atoms, ions | Oxidation and removal of organic films |
| Food Processing/Decontamination of CBW Agents/Medical Equipment Sterilization | O , O_2^+ , H , OH : chemical reactions initiated by plasma chemistry | Destruction or denature of pathogens, prions; chemical destruction of toxins |
| Water/Wastewater Treatment | O , O_2^+ , O_3 , OH : chemical reactions initiated by plasma chemistry | Removal or destruction of water contaminants, pathogens, and reduction of biological oxygen demand (BOD) |

Plasma Characteristics

In the most general cases, the plasma is used as a chemical reactor, to produce short-lived, active species that are formed by interaction of plasma electrons with the feed gas present in the plasma. This generality applies whether the plasma is produced in a vacuum or at atmospheric pressure.

Ions are always present in any plasma. Ions may enhance the surface reactivity contributed by active neutrals, such as in etching processes², or they may cause unwanted side effects, such as surface damage³. As such, design of materials-processing methods requires a means to either increase or reduce the amount of ion interaction with the surface. In many cases, ions impart significant energy to a surface. This helps to drive a chemical reaction, or may even bring about a purely physical reaction process, such as sputtering of target material for metallic coatings. The use of combined, chemical plus physical, reactions are common in many plasma process steps. Note that a significant benefit of atmospheric-pressure plasma processing results from the greater control available

for selecting chemical or physical processes that result from ion interaction with the surface. This is because ion recombination and loss rates at high pressure are much faster than in vacuum.

Plasmas are generally classified as either thermal or nonthermal. Thermal plasmas are characterized by an equilibrium, or a near equality, between the three components of the plasma: electrons, ions, and neutrals: (*i.e.*, $T_e \approx T_i \approx T_n$). Thermal plasmas are always “hot”; temperatures of several thousand degrees are not unusual. Flames, arc discharges, and nuclear explosions are examples of thermal plasmas. While these plasmas have uses in waste treatment and sintering, they are not well suited for most materials-processing applications because of their destructive nature.

Nonthermal plasmas, in contrast, are characterized by a large difference in the temperature of the electrons relative to the ions and neutrals. Because the electrons are extremely light, they move quickly and have almost no heat capacity. In these plasmas, $T_e \gg T_i \approx T_n$. Ionization is maintained by the impact of electrons (which may have temperatures ranging from

0.1 to more than 20 eV) with neutral species, which produces additional electrons and ions. These plasmas are typically maintained by the passage of electrical current through a gas. The low temperatures of nonthermal plasmas makes them well suited for materials-processing applications. However, unlike thermal plasmas, nonthermal plasmas generally have required vacuum or low-pressure operation. Table 2 summarizes the characteristics of thermal and nonthermal plasmas.⁴

Table 2. Comparison of Properties of Thermal and Nonthermal Plasmas

| | Thermal Plasma | Nonthermal Plasma |
|---|---------------------------------|--------------------------------|
| Pressure (atm) | low pressure to many atm. | typically low pressure |
| Electron/ion Density (cm^{-3}) | 10^{12} – 10^{19} | 10^8 – 10^{13} |
| Electron Temperature (K) | 5,000–500,000 (0.5–50 eV) | 1,000–50,000 (0.1–5 eV) |
| Ion/Neutral Temperature (K) | 5,000–30,000 | 100–1,000 |
| Energy Source | electrical, nuclear, combustion | electrical, ionizing radiation |

Atmospheric-Pressure Plasma Sources

Besides the aforementioned use of nonthermal plasmas in vacuum environments, several kinds of atmospheric-pressure plasmas also are known.⁵ Figure 3 illustrates some of the varieties of atmospheric-pressure plasmas. The so-called “dielectric barrier” discharge, Figure 3a, utilizes a dielectric covering over one or both of the electrodes of which one is typically low-frequency, radio-frequency (rf), or alternating-current (ac) driven while the other is grounded. The purpose of the dielectric film is to rapidly terminate the arcs that form in the potential field between the two electrodes. The discharge consists of a multitude of rapidly forming and equally rapidly terminated arcs that fill the volume between the electrodes. Materials processing may be done using the ozone generated (in the case of an air or oxygen feed gas) or even by passing the substrate material—assuming it is a dielectric—within the discharge region between the electrodes.

The corona discharge, shown in Figure 3b, is a nonarcing, nonuniform plasma that ignites adjacent to the high electric field generated by the sharp points of the electrodes. To prevent arcing, no

grounded surface can be near these field emission points, so the discharge is, by nature, nonuniform: plasma density drops off rapidly with increasing distance from the electrode.

The plasma torch, shown in Figure 3c, is often confused with the atmospheric-pressure plasma jet to be described next. Unlike the other plasma sources shown in this figure, the plasma torch is a thermal plasma characterized by a high ion temperature \approx electron temperature. This source makes use of its very high gas temperatures for materials-processing applications, primarily for chemical-waste destruction, deposition of ceramic coatings, and sintering applications.

The fourth source, shown as Figure 3d, is the atmospheric-pressure plasma jet (APPJ). It is similar to the plasma torch in some respects but is a true nonthermal plasma, as demonstrated by the vast difference in ion and electron temperatures. The APPJ source produces a stable, homogeneous and uniform discharge at atmospheric pressure using 13.56 MHz rf power and a predominate fraction of helium feed gas. Unlike

the silent discharge, the APPJ operates without any dielectric electrode cover, yet is free of filaments, streamers, and arcing. The gas temperature of the discharge is typically between 50 and 300°C, so thermal damage to materials is easily avoided.

Figure 4 shows a photograph of the APPJ in operation. As described in the next section, this so-called cylindrical version of the plasma jet is only one kind of APPJ source. Several different variations exist. These different versions provide added benefit for certain applications. We have previously published several technical articles on the plasma physics and chemistry of this unique source.^{6,7,8,9,10,11,12}

In the design shown in Figures 3 and 4, helium feed gas (^a99%) mixed with a small amount of reactive gas (typically 1%–3% oxygen) enters the annular volume formed between the rf-powered electrode (along the longitudinal axis of the source) and the outer, grounded metal tube. One novel aspect of this APPJ source is that the discharge is formed in this small volume—which typically has insufficient room for immersion of the workpiece or substrate, but the

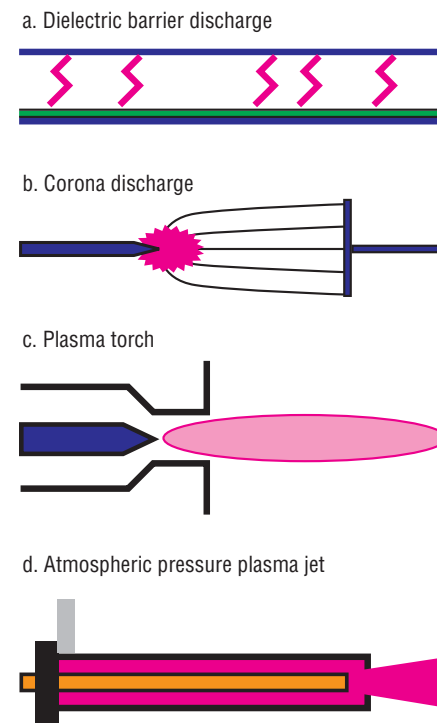


Figure 3. Four different kinds of atmospheric-pressure plasma sources.

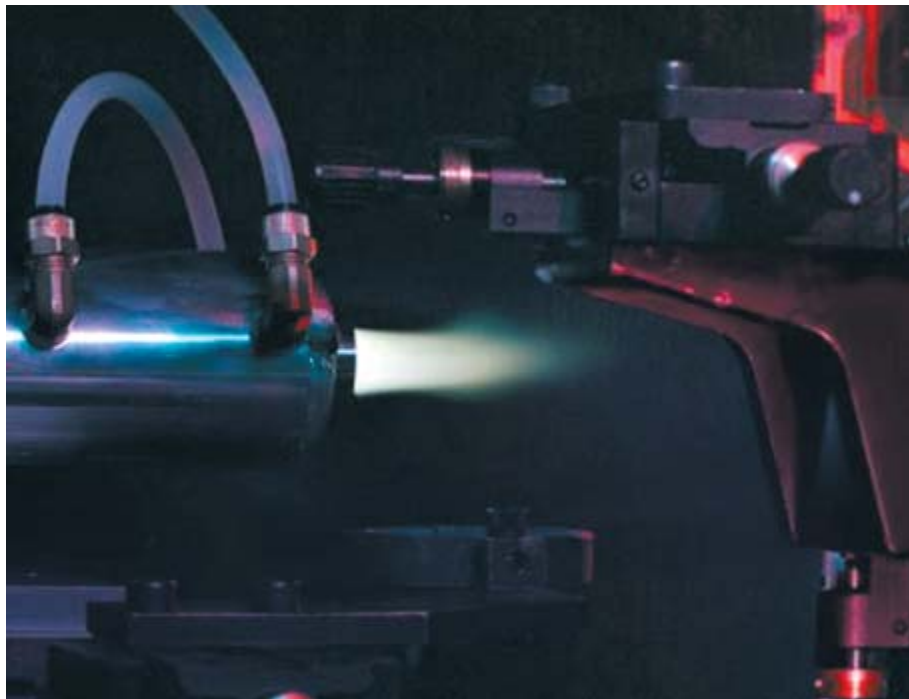


Figure 4. Operation of a cylindrical version of the APPJ. Note the effluent stream of reactive chemical species that exits from the end of the APPJ source.

Table 3. Typical Process Parameters for the Cylindrical APPJ Source

| | |
|--|--------------------------------------|
| RF frequency | 13.56 MHz |
| RF power | 250 W |
| Plasma power density | 35 W/cm ³ |
| Discharge voltage | 320 V _{rms} |
| Electron density | ~10 ¹¹ cm ⁻³ |
| Electron temperature | ~2-3 eV |
| He flow | 92 slpm |
| O ₂ flow | 0.72 slpm |
| Gas velocity ^{a, b} | 43 m/s |
| Effluent temperature ^b | 150°C |
| Ozone density ^b | ~1x10 ¹⁵ cm ⁻³ |
| Atomic oxygen density ^b | ~5x10 ¹⁵ cm ⁻³ |
| Metastable oxygen (O ₂ ¹ Δ _g) density ^b | ~5x10 ¹⁵ cm ⁻³ |
| ^a using 8 mm diameter nozzle | |
| ^b measured or estimated at nozzle exit | |

active chemical species formed by the plasma rapidly exit the source and can impinge downstream on the workpiece.¹³ In this way, the substrate is mostly exposed to active neutrals and radicals, rather than ions. The absence of ion chemistry in the downstream flow increases chemical selectivity and

reduces surface damage. Of course, this design also uses large quantities of helium feed gas, because slow flow rates result in longer transit times, which favors the recombination or loss of the active, chemical species. Table 3 shows typical process parameters for this source used under normal conditions.

Atmospheric-Pressure Plasma Jet Sources and Applications

The cylindrical design shown in Figures 3d and 4 represents only one variation of the APPJ-source technology. In some applications, especially where large area surface treatment is needed, it may be more desirable to use a similar design, but one in which flat, parallel, planar electrodes are used. A clear advantage of this approach is that the electrode size may be readily scaled up. Because the electrodes are securely held in place on either side, large areas (*i.e.*, 1 m² or more) may be achieved, while still keeping the gap between the electrodes precise. Figure 5 shows the design of a “flat jet” and a photograph of this source in operation. By placing the rf electrode between the two (outer) grounded electrodes, we can achieve dual-source operation, as well as provide a safer approach to handling the flat jet.

The flat jet also presents an interesting process opportunity for high-pressure plasma processing. It may be used in either of two modes: 1) downstream operation, as shown in Figure 5a, or 2) for in-situ treatment of materials, accomplished by immersing the material on, or between, the rf-driven and grounded electrodes. Silicon wafers

are ideally suited for the latter application because of their thin dimensions, as well as other materials, such as textiles. Even water or wastewater may be channeled to flow along the surface of an electrode in order to expose it to the plasma. With the exception of wafer treatment, these opportunities would clearly be infeasible for vacuum-based plasma processing—not only because of the difficulty of feeding these materials into a vacuum chamber, but also because of the vapor pressure of the workpiece.

Figure 6 shows various means by which the APPJ source has been employed. All have similar properties and characteristics: *i.e.*, use of helium to maintain a nonthermal plasma, low temperature processing, and high flux of reactive species impinging upon the substrate.

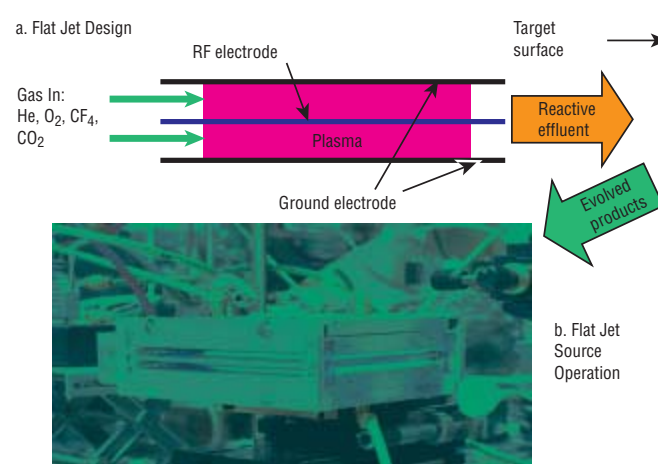


Figure 5. A schematic drawing (a) of the flat jet and a photograph (b) of the same in operation.

Comparison of the APPJ Technology to Other Plasma Sources

All plasma processes have their relative advantages and disadvantages. For example, the highly collisional nature of the APPJ discharge makes it unlikely that this plasma would be used for directional etching of silicon, whereas a vacuum-based plasma serves this purpose well. Collisions are also responsible for the rapid removal of ions in the effluent stream as it exits the source of the APPJ, so this same phenomenon acts to reduce damage in photoresist ashing processes.

Still, a problem that APPJ applications must face is the high use rate of helium feed gas. Helium is used to stabilize the discharge, and for electrode cooling, by virtue of its high thermal conductivity. For this reason, most commercial applications that employ APPJ technology will have to use equipment to recirculate and repurify the feed gas. While this slightly increases the capital cost of the equipment, the operating costs are greatly reduced. Complete systems for filtering helium are commercially available. A helium reprocessing system is indicated in Figure 6d. Not only do these systems reduce COO by reusing the helium carrier gas, but

they also increase the domain of potential applications by moving the left axis of the large box in Figure 1 further to the left—enabling applications that have lower material unit value. We have demonstrated this helium recovery system in a system designed for decontamination of materials having chemical or biological warfare agents, another potential use for the plasma jet.¹⁴

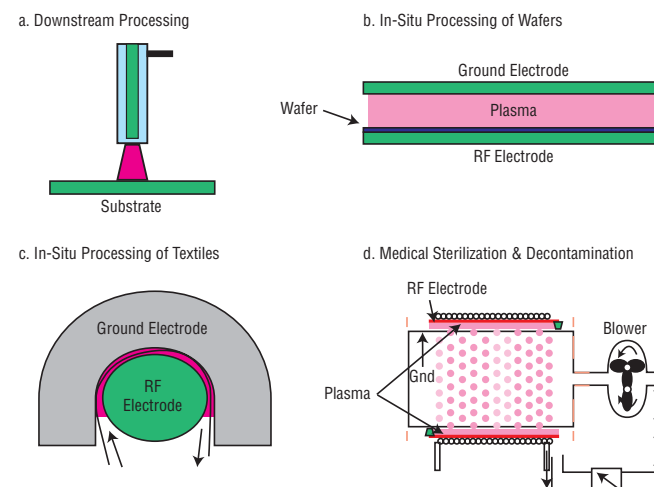


Figure 6. Variations in use of the APPJ technology and different source designs.

Summary and Outlook

Cold, atmospheric-pressure plasmas have the potential to displace many traditional, vacuum-based, plasma-processing practices as well as open up entirely new plasma applications. This results from its ability to inexpensively treat low-value items as well as materials incompatible with vacuum processing owing to their high vapor pressure or cumbersome shape or size. Commercial possibilities abound and the University of California (UC) is currently in the process of licensing this technology out to the private sector. In terms of applications of Department of Energy (DOE) interest, we have primarily been developing these plasmas for chemical, biological, and nuclear decontamination.

DOE NN-20, now part of the newly formed National Nuclear Security Administration (NNSA), has been supporting research to strengthen our nation's defense against chemical and biological terrorism through its Chemical/Biological National Security Program (CBNP). Our effort is aimed at providing domestic emergency responders with a means to quickly neutralize these horrific weapons of mass destruction through oxidation by plasma-activated gases. The

primary advantages of this technology for chemical/biological decontamination is that it is dry and relatively nondestructive to most materials, hence it can be used on "sensitive" equipment such as electronics and optics for which there is currently no suitable decontamination option. A plasma decontamination chamber, similar to the one depicted in Figure 6d, is currently undergoing "live agent" testing on chemical nerve agents, such as VX and Sarin, and blister agents, such as Mustard, at the Army's Dugway Proving Ground. Ultimately, this device may be commercialized as a low-temperature medical sterilizer to help displace the health care industry's current standard of ethylene oxide, a flammable, toxic, and environmentally unsound gas. We are also developing methods to be used in a plasma decontamination jet, a hand-held wand that can decontaminate sensitive equipment in-situ while installed at facilities such as control centers for commercial communications, power, and transportation facilities as well as conventional office space. Naturally, these technologies have military defense applications as well.

Under DOE's Environmental Management Science Program (EMSP), we have also been developing actinide decontamination in collaboration with UCLA's Chemical Engineering Department. By adding fluorine containing gases, such as CF_4 or NF_3 , to the APPJ's helium stream we can also produce atomic fluorine capable of etching the actinides plutonium and uranium. Reaction with the fluorine produces volatile byproducts which can then be trapped in filters. This allows one to take a large item considered transuranic (TRU) waste, such as a glove box, and convert it to low-level radioactive waste. Only a small filter then needs to be disposed of as TRU waste, allowing the DOE to save large sums of money through volume reduction. We are currently optimizing the process on actinide surrogates, such as tantalum, and designing a system to be used in a plutonium decontamination demonstration in the CMR facility next fiscal year.

The atmospheric-pressure plasma jet, invented at the Laboratory in 1995 and winner of an R&D 100 Award in 1999, represents a new direction for the plasma processing of materials. The ability to dispense

with the vacuum chamber will make plasmas much more attractive in numerous applications that range from surface treatments such as cleaning, etching, decontamination, thin-film deposition, and surface modification to volume processing of gases and liquids. Recent improvements, such as replacement of the helium carrier gas with cheaper and more readily available gases such as argon, steam, and even air, continue to make this technology even more practical. Of course, developments such as these necessitate basic research that leads to a fundamental understanding of this relatively new realm of plasma physics. By spinning-off this technology to the private sector, the UC stands to generate a substantial income stream which can be reinvested in research and development, further strengthening our intellectual-property portfolio in atmospheric-pressure plasmas.

References/Further Reading

- ¹ C. J. Mogab in, *VLSI Technology*, S. M. Sze Ed., (McGraw Hill, New York, 1983), pp 303–346.
- ² J. W. Coburn, *Plasma Chemistry and Plasma Processing* 2, 1 (1982).
- ³ K. F. You, M. C. Chang, C. Y. Wu, *IEEE Trans. Elect. Dev.* 45, 239 (1998).
- ⁴ M. A. Lieberman and A. J. Lichtenberg, *Principles of Plasma Discharges and Materials Processing*, (Wiley-Interscience, New York, 1994), pp 6–10.
- ⁵ A. Schuetze, J. Y. Jeong, S. E. Babayan, *et al.*, *IEEE Trans. Plasma Sci.* 26, 1685 (1998).
- ⁶ S. E. Babayan, J. Y. Jeong, V. J. Tu, *et al.*, “Deposition of Silicon Dioxide Films with an Atmospheric-Pressure Plasma Jet,” *Plasma Sources Science and Technology* 7, 286–288 (1998).
- ⁷ J. Y. Jeong, S. E. Babayan, V. J. Tu, *et al.*, “Etching Materials with an Atmospheric-Pressure Plasma Jet,” *Plasma Sources Science and Technology* 7, 282–285 (1998).
- ⁸ J. Y. Jeong, J. Park, I. Henins, *et al.*, “Reaction Chemistry in the Afterglow of an Oxygen-Helium, Atmospheric-Pressure Plasma,” *Journal of Physical Chemistry A* 2000, 104 (34) 8027–8032 (2000).
- ⁹ J. Park, I. Henins, H. W. Herrmann, *et al.*, Discharge Phenomena of an Atmospheric Pressure Radio-Frequency Capacitive Plasma Source,” *Journal of Applied Physics* 89, 20–28 (2001).
- ¹⁰ V. J. Tu, J. Y. Jeong, A. Schutze, *et al.*, “Tantalum Etching with a Nonthermal Atmospheric-Pressure Plasma,” *Journal of Vacuum Science and Technology A* 18, 2799–2805 (2000).
- ¹¹ J. Park, I. Henins, H. W. Herrmann, *et al.*, “Gas Breakdown in an Atmospheric Pressure Radio-Frequency Capacitive Plasma Source,” *Journal of Applied Physics* 89, 15–19 (2001).
- ¹² J. Park, I. Henins, H. W. Herrmann, *et al.*, “An Atmospheric Pressure Plasma Source,” *Applied Physics Letters* 76, 288–290 (2000).
- ¹³ US Patent No. 5,961,772 issued Oct. 5, 1999.
- ¹⁴ H. W. Herrmann, I. Henins, J. Park *et al.*, “Decontamination of Chemical and Biological Warfare (CBW) Agents Using an Atmospheric Pressure Plasma Jet,” *Physics of Plasmas* 6, 2284–2289 (1999).